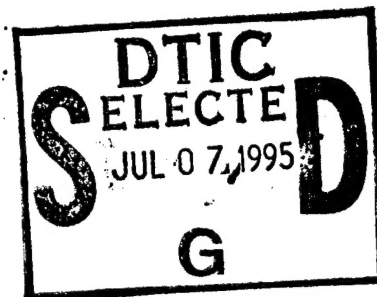


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WELL-DEFINED POLYMERS OBTAINED THROUGH THE USE OF CONTROLLED  
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TRANSFER AGENTS.

by

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# Well Defined Polymers Obtained Through the Use of Controlled Radical Polymerization: The Use of Alkyl Iodides as Degenerative Transfer Reagents

Scott G. Gaynor, Jin - Shan Wang, and Krzysztof Matyjaszewski\*

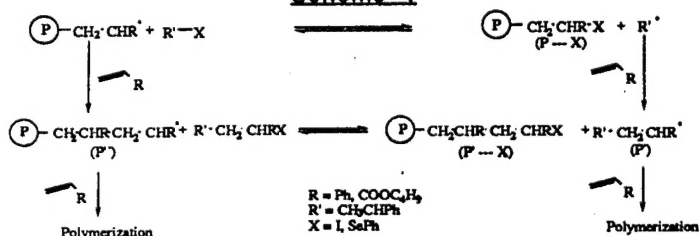
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## Introduction

Controlled polymerizations are usually realized through the use of living polymerizations, in which there is an absence of chain breaking reactions, i. e., termination or transfer. Most notably this is done through anionic pathways,<sup>1</sup> however, cationic pathways have also been used. Besides the stringent conditions required for these polymerizations, i. e., complete absence of water, the major drawback to these systems is the limited scope of monomers which can be used. In contrast, the number of vinyl monomers which can be polymerized radically is vast. Radical polymerizations can be performed in environmentally friendly water, and the lone requirement is the exclusion of oxygen, which is easily accomplished. It is the combination of ease of polymerization and the large number of monomers capable of radical polymerization which drives one to develop controlled free radical polymerizations.

Although it is impossible to eliminate termination in radical polymerizations, the contribution of termination can be significantly lowered under appropriate conditions. Three methods have been recently reviewed, and one of these, degenerative transfer, is the subject of this communication.<sup>2</sup> In degenerative transfer, Scheme 1, a transfer agent,  $R' - X$ , reacts with a propagating radical to form a dormant polymer chain,  $P - X$ . The new radical,  $R'$ , can then reinitiate polymerization. Because of this, the number of polymer chains is equal to the concentration of the transfer agent. The newly formed polymer chain,  $P'$ , can then react with the dormant polymer chain,  $P - X$ , to form  $P' - X$  and  $P$ . This is significantly different from degradative transfer, used in typical telomerization reactions, due to the unreactivity of the dormant polymer chains after initial reaction with the transfer agent. Similarly, iodine and selenium compounds have been used successfully in organic synthesis in radical addition reactions to various vinyl compounds.<sup>3</sup>

Scheme 1



## Results and Discussion

Optimally, the exchange reaction between the dormant and active radical species should be a thermodynamically neutral reaction. In order for this to be obtained, the transfer agent should resemble the polymer chain end. The compound which was initially employed was 1 - phenylethyl iodide, 1 - PEI. This compound was synthesized by Markovnikov addition of HI to styrene in the presence of a phase transfer catalyst.<sup>4</sup>

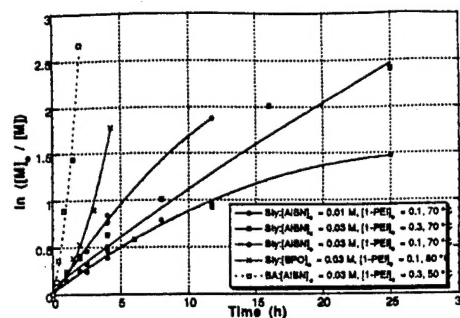


Fig. 1 Kinetics of bulk polymerization of styrene, Sty, and butyl acrylate, BA, at various conditions.

Figure 1 shows the kinetics of the bulk polymerization of styrene under various conditions and also the polymerization of butyl acrylate. The polymerization of butyl acrylate was carried out at 50 °C to lower the rate of polymerization; the rate of polymerization was too fast at 70 °C. As can be seen in Figure 1, this polymerization had the highest rate of polymerization. The bulk polymerization of butyl acrylate also exhibited an accelerated rate at higher conversions. This may be due to an increase in the viscosity of the polymerization system which prevented termination in a manner similar to the Trommsdorff effect.

The polymerization of styrene at 80 °C initiated by BPO showed that the rate of polymerization increased with time as the reaction reached higher conversions. This, again, was due to the reasons cited above.

When the initiator AIBN was used, the plots were linear with the exception of when AIBN was used in the concentration of 0.01M. At this concentration, the rate of polymerization decreased. This was due to the fact that the amount of AIBN was substantially reduced when the styrene polymerization had reached high conversions. After 20 hours, the concentration of AIBN would have been 1 / 16 th of the original value, resulting in a rate of polymerization one - fourth the original. The apparent linearity of the kinetic plots at higher initiator concentrations, may be due to the simultaneous actions of both effects, i. e., rate reduction and rate acceleration.

Increasing the amount of transfer agent, 1 - PEI, resulted in a slower polymerization. As can be seen in Figure 1, when  $[1 - \text{PEI}]_0 = 0.1 \text{ M}$  was used, the reaction was 63 % complete in twelve hours, while the reaction using  $[1 - \text{PEI}]_0 = 0.3 \text{ M}$  required sixteen hours to reach similar conversions. This may be due to the generation of a small amount of  $\text{I}_2$  which acts as an inhibitor in radical polymerizations.

More importantly, the molecular weight of the polymer increased with conversion and approached the theoretical value of  $\text{DP}_n = \Delta[M] / [R' - X]_0$ , Figure 2. When no transfer agent was used, the molecular weight of the polymer,  $M_n \sim 60,000$ , did not increase with conversion. The observation that the molecular weight was higher than predicted at the outset indicated that the rate of exchange of iodine between the propagating radical and the transfer agent was slow in comparison to the rate of propagation. The polydispersities were  $< 1.6$  even at conversions greater than 90%. This is in sharp contrast to the polymerization of styrene without the transfer agent,  $M_n / M_w > 2$ .

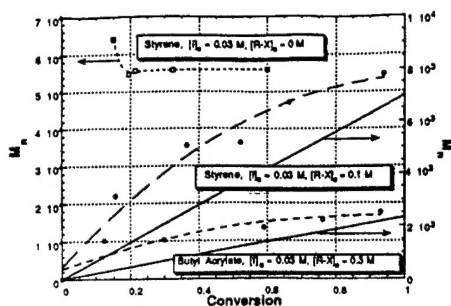


Fig. 2 Molecular weight dependence upon conversion for the bulk polymerization of styrene and butyl acrylate at 70 °C.  $[I] = \text{AIBN}$ ,  $[R-X] = 1\text{-Phenylethyl iodide}$ .

Also, as can be seen from Figure 2, butyl acrylate has been successfully polymerized radically using 1 - PEI. Block copolymers of styrene and butyl acrylate have been prepared.

The rates of polymerization increased with temperature. At 70 and 90 °C, there was no significant effect on the evolution of molecular weight. However, when the polymerization was carried out at 50 °C, the molecular weights were higher than at the higher temperatures indicating that transfer between the propagating radical and the transfer agent was slower.

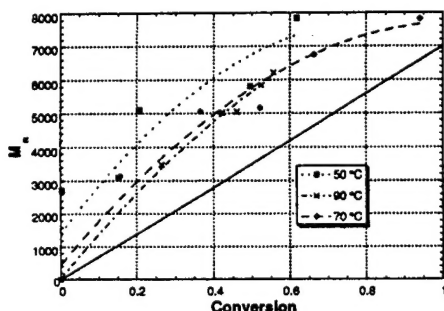


Fig. 3  $M_n$  dependence on conversion in the bulk polymerization of styrene at various temperatures.  $[AIBN]_0 = 0.03 \text{ M}$ ,  $[1\text{-PEI}]_0 = 0.1 \text{ M}$ .

Various transfer agents were used to explore the effect of  $R'$  on the control of molecular weight. The following iodine compounds were used in addition to 1 - phenylethyl iodide: perfluorohexyl iodide, perfluoroisopropyl iodide, iodoacetonitrile, isopropyl iodide, *n* - propyl iodide and phenyl iodide. Of these, only phenyl iodide showed no control of molecular weight versus conversion. Isopropyl iodide and *n* - propyl iodide did show an increase in molecular weight but apparently the molecular weight was governed by concentration of the initiator and not by the transfer agent, Figure 4.

Figure 5 shows the dependence of molecular weight with conversion for the others. As can be seen, the perfluorinated compounds led to molecular weights higher than 1 - phenylethyl iodide and iodoacetonitrile. This may be connected to the stability of the iodo compounds. The stronger the carbon iodine bond, the slower the rate of reaction between the propagating radical and the transfer agent, and thus resulting in higher molecular weights. The use of iodoacetonitrile led to results similar to 1 - phenylethyl iodide.

The polydispersities of the polymers were typically in the range of 1.4 - 1.6. These were relatively low in comparison to the blank polymerization which had  $M_w / M_n > 2$ . The polydispersities, however, were higher than what are usually found for a living polymer indicating that termination was occurring in the polymerization system and that exchange between the dormant and active species was not fast.

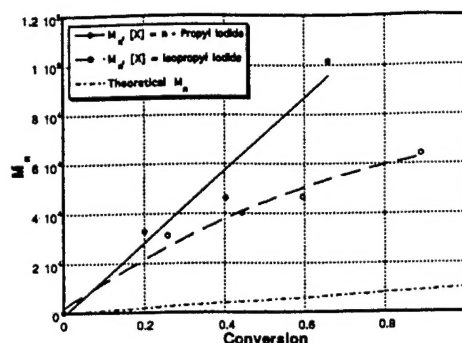


Fig. 4 Dependence of molecular weight upon conversion for the polymerization of styrene in the presence of *n* - propyl iodide and isopropyl iodide at 70 °C.  $[AIBN]_0 = 0.0086 \text{ M}$ ,  $[X]_0 = 0.086 \text{ M}$

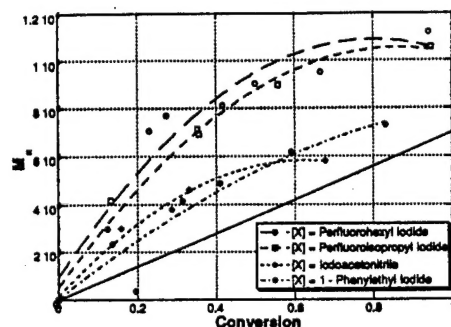


Fig. 5 Dependence of  $M_n$  on conversion for the bulk polymerization of styrene at 80 °C.  $[BPO]_0 = 0.03 \text{ M}$ ,  $[X]_0 = 0.1 \text{ M}$

## Conclusions

By using the alkyl iodide, 1 - phenylethyl iodide, the controlled radical polymerization of styrene, and also butyl acrylate, has been achieved. This has afforded a straightforward method of synthesizing polymers with molecular weights according to the equation  $DP_n = \Delta[M] / [R' - X]_0$ . This method also allowed for the synthesis of polymers with functionalized end groups by radical polymerization. Polymer molecular weights were not effected by initiator, but were influenced by the strength of the carbon iodine bond in the transfer agent.

## Acknowledgments

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